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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

NOTE ON THE RATE OF DEHYDRATION OF CRYSTALLIZED SALTS.

By Theodore William Richards.

Presented May 12, 1897.

In the course of the investigation of the atomic weights of barium and strontium, a few observations were made upon the rate of dehydration of several of the salts of these metals. These observations supplement the work of Lescœur,* Roozeboom,† and others, concerning the vapor tension of water contained in crystallized salts. It was found that the rate of the withdrawal of water by means of a constant desiccating agent varied very greatly with different substances, as well as with different hydrates of the same substance. Baric chloride, for example, exposed to a dry atmosphere at first effloresces with great rapidity, and then, after it has lost one of its molecules of water of crystallization, continues to be dehydrated at a much slower rate. This is nothing more than was to be expected, for the rate of dehydration must be approximately proportional to the tension of the aqueous vapor in the salt, provided that the aqueous vapor is equably removed from the surrounding atmosphere. It is obvious, therefore, that successive weighings of any material which is gradually efflorescing may furnish a useful clue to the relative vapor tensions of the successive molecules of crystal water contained in that substance.

As an example of the definiteness of the change of rate, one of several concordant experiments upon baric cloride may be cited. 1.2223 grams of the finely powdered crystallized salt were weighed out in a small crucible; and with this substance was mixed a small amount of pure washed and ignited asbestos, in order to allow freer circulation of air. This precaution was not necessary for the success of the experiment, although it had been found to increase somewhat the sharpness in the change in the rate of dehydration. The crucible was now placed in a small desiccator containing phosphoric oxide, and the whole was placed in a thermostat maintained at 30°. From time to time the crucible was rapidly weighed, the phosphoric anhydride being stirred in order to expose a new surface to the moist air. The results of this experiment are recorded below.

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* Ann. Chim. Phys., (6.), XIX. 533, XXI. 511, (7.), II. 78.

† Comptes Rendus, CX. 134; Zeit. Phys. Ch., II. 449; also IV. 31, etc. etc.

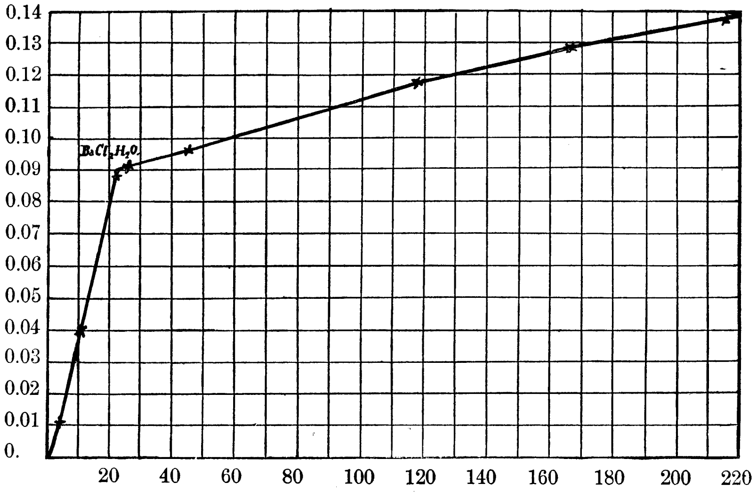
Rate of Dehydration of Baric Chloride.

Time (from beginning) in Hours.	Time (from previous weighing) in Hours.	Total Loss (in Grams).	Loss between two weighings (in Grams).	Rate of Loss — Milligrams per Hour.
0	0	0	0	
0.5	0.5	.0010	.0010	2.0
4.3	3.8	.0109	.0099	2.6
11.0	6.7	.0400	.0291	4.3
22.8	11.8	.0886	.0486	4.1
26.7	3.9	.0914	.0028	0.72
45.8	19.1	.0964	.0050	0.26
118	72.2	.1174	.0210	0.29
166	48.0	.1284	.0110	0.23
214	48.0	.1374	.0090	0.19

After several days more, the salt had lost very nearly all of its crystal water, although the last portions, which must have been in the centre of the various masses constituting the powder, naturally left more and more slowly. Exposed to the somewhat moist air of the laboratory, the salt regained in a few days all the water which it had lost.

The only remarkable thing about this rather commonplace experiment was the suddenness of the change in the rate after the first molecule of water of crystallization (0.0900 grams) had gone. Graphic representation will make the point clearer. In the accompanying diagram, the loss of water (in grams) is plotted vertically, while time (in hours) is plotted horizontally.

Rate of Dehydration of Baric Cloride.



The sharp angle occurs exactly at the point corresponding to $BaCl_2H_2O$.

A number of other salts also were experimented upon, — those with little water of crystallization usually behaving in the same general manner as baric chloride, while those with much water of crystallization (such as sodic carbonate) gave less angular curves, in which the various hydrates were only slightly, if at all, perceptible. It is well known that all the hydrates are not necessarily formed during such a dehydration. In order to obtain a sharp change with any salt, it is manifest that one must use a desiccating agent which does not remove the water much faster from the surface than it can be supplied by diffusion from below. Hence from such a substance as sodic carbonate one obtains more satisfactory results by using diluted sulphuric acid instead of phosphoric oxide in the desiccator; by no means a new idea. For any given case, the aqueous vapor tension of the desiccating agent should be not much less than that of the salt during the removal of the water corresponding to the second limb of the desired curve.

It is convenient to have at hand for this purpose a table giving the approximate strength of sulphuric acid necessary to obtain a given tension of aqueous vapor at a given temperature. The data for such a table may be found in the work of Regnault,* and Lunge and Isler.†

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* Ann. Chim. Phys., (3.), XV. 179. Landolt und Börnstein, Tabellen, 1894, p. 65.

† Z. Angew. Chem., 1890, p. 129. Landolt und Börnstein, p. 196.

Below is given a partial table of this sort, which suffices for ordinary work with crystallized salts. It was obtained from the data above mentioned by graphic interpolation. The specific gravities of diluted sulphuric acid given in the last three columns are taken at 15°, and referred to water at 4°; — sulphuric acid of any strength given below placed in a desiccator kept at the temperature given at the top of the column, is then capable of yielding aqueous vapor at a tension found in the first column. Since the curves corresponding to Regnault's data are not quite regular, these values are only near approximations.

Specific Gravities of Sulphuric Acid capable of yielding Aqueous Vapor at various Tensions.

Tension of Aqueous Vapor.	20° C.	25° C.	30° C.
0	1.838	1.838	1.838
0.25	1.750	1.763	1.772
0.50	1.693	1.710	1.726
1.00	1.642	1.666	1.688
1.50	1.603	1.629	1.652
2.00	1.570	1.600	1.629
2.50	1.538	1.575	1.605
3.00	1.510	1.550	1.589
4.00	1.470	1.513	1.555
5.00	1.434	1.482	1.530
6.00	1.404	1.455	1.504
7.00	1.378	1.429	1.482
8.00	1.355	1.405	1.455
10.00	1.308	1.368	1.430
15.00	1.16	1.28	1.353

This table is also of practical use in preparing dry crystallized substances. For instance, crystallized oxalic acid, so much used in making standard solutions, is best prepared by placing the powder over sulphuric acid of specific gravities 1.20 to 1.50; for the crystallized substance does not lose an essential amount of water at 22° in an atmosphere containing aqueous vapor at a tension of 4 millimeters; while the aqueous vapor tension of its saturated solution is more than 15 millimeters.*

It is almost needless to call attention to the fact, recognized as a matter of course by any one who has especially studied the subject of water of crystallization, that the temperatures of dehydration given in text-books are often wholly indeterminate and almost meaningless, since the tensions of the aqueous vapor in the surrounding atmosphere are frequently not given. Much of our literature upon this subject needs a systematic revision.

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* W. D. Bancroft has recently published statements bearing upon this subject, some of which are founded upon slight experimental evidence, under the title "Solids and Vapors." (The Physical Review, Ithaca, N. Y., Vol. III. p. 401, and The Journal of Physical Chemistry, Ithaca, N. Y., Vol. I. p. 345.)

CAMBRIDGE, MASS., May, 1897.